Application of the Time-Fractional Diffusion Equation to Describing the Methanol Transport in the Catalyst Grain for Methanol-to-Olefin Reaction

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Summary. Methanol mass transfer through the catalyst grain for methanol-to-olefin reaction was studied. We demonstrate that methyl alcohol transport is qualitatively and quantitatively described by the time-fractional diffusion equation. The measured value of the fractional derivative order corresponds to the super-diffusive regime of transport, which is considerably faster comparing to standard diffusion. The obtained results are of great importance because they provide an approach to improving the productivity of the commercially important methanol-to-olefin reaction by simple controlling the fast transport regime of the chemical agents.

Objectives

Anomalous diffusion in the porous media is very important for processes that include transport stages, e.g. heterogeneous catalysis, because depending on the value of the fractional order this kind of transport may occur slower or faster comparing to the standard diffusion. Anomalous diffusion may be described by the time-fractional diffusion equation, which accounts temporal nonlinearity of the mean square displacement of the diffusing particles. H-ZSM-5/alumina extrudates are typical catalysts for methanol-to-olefin reaction. The latter is commercially used for light olefins production, e.g. ethylene and propylene, from methanol. It is possible to increase the effectiveness of the process by increasing the mass transfer rate. This may be achieved by providing the fast super-diffusive regime of reagents transport in the pores of the catalyst grain. Therefore, investigating the mass transport peculiarities of different chemicals in the solid porous media is important for better understanding the fundamentals of the heterogeneous catalysis.

Asymptotic solutions of the time-fractional diffusion equation

Initial and boundary conditions that concern the real experimental conditions are represented as: $C(x, 0) = C_0(x) = const$, $\partial C(0, t)/\partial x = 0$. Using the asymptotic Green's functions for the time-fractional diffusion equation provided in Ref. [1] for the given initial and boundary conditions the solutions of the time-fractional diffusion equation for small and large times at an upper boundary L, corresponding to the catalyst grain thickness, are derived respectively:

$$C(L, t) = C_0 \cdot \frac{L}{\sqrt{\frac{\pi \cdot K \cdot t^\alpha}{\Gamma(m + \alpha)}}} \tag{1}$$

$$C(L, t) = C_0 \cdot \frac{L^2 \cdot \sqrt{2 \cdot \pi}}{K \cdot t^\alpha \cdot \Gamma(m - \alpha)} \tag{2}$$

Where α is a fractional order, m is 1 for $0 < \alpha < 1$, and m is 2 for $1 < \alpha < 2$, $\Gamma(z)$ is Euler gamma function. The obtained solutions may be linearized in the logarithmic coordinates as:

$$\ln\left[\frac{C(L, t)}{C_0}\right] = \ln\left[\frac{L}{\sqrt{\frac{\pi \cdot K}{\Gamma(m + \alpha)}}}\right] - \frac{\alpha}{2} \cdot \ln t \tag{3}$$

$$\ln\left[\frac{C(L, t)}{C_0}\right] = \ln\left[\frac{L^2}{K \cdot \Gamma(m - \alpha)}\right] - \alpha \cdot \ln t \tag{4}$$

As it follows from Eqs. (3) – (4) measuring the linear equations parameters by fitting the experimental data provides enough information about the transport regime and allows determining the values of the diffusion constant and the order of the temporal derivative.

Experimental techniques

H-ZSM-5/alumina catalyst grain with alumina/zeolite ratio equal to 1/1 was prepared according to the well-known extrusion method. Obtained porous grain's structure was characterized by the low-temperature nitrogen adsorption-desorption isotherm, which was recorded using Sorptomatic 1990 instrument at 77°K. Low-temperature nitrogen adsorption-desorption isotherm of the ZSM-5/alumina grain is demonstrated in Fig. 1. BET surface area calculated according to the isotherm is $272 m^2/g$; pore volume is $0.2217 cm^3/g$; BJH pore diameter is 3.9nm; external surface area is $21 m^2/g$; micropore volume is $0.0396 cm^3/g$; mesopores surface area is $177 m^2/g$.

Methanol transfer inside the porous H-ZSM-5/alumina grain was investigated using commercial LHM-72 gas chromatograph with the flame ionization detector. The chromatograph column was replaced by the diffusion cell. The

detailed description of the diffusion cell design may be found in our previous report [2]. The study was carried out for the following experimental conditions. The gas-carrier (argon) flow rate was $30 cm^3/min$; temperature inside the diffusion cell was 70°C. Methanol amount injected into the diffusion cell was 0.3µl. Grain thickness was 2mm.
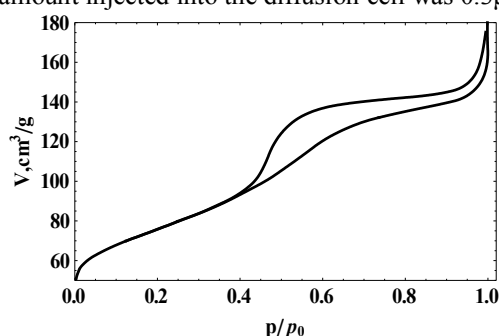

Fig. 1. The nitrogen adsorption-desorption isotherm at 77K

Experimental data analysis

The experimental data in the logarithmic coordinates fitted by the asymptotic solutions of the time-fractional diffusion equation according to Eqs. (3) and (4) are demonstrated in Figs. 2a and 2b for small and long times respectively. As it follows from the data presented in Figs. 2a and 2b the experimental data of the methanol transport through the pores of the catalyst grain are fitted by the corresponding time-fractional asymptotic linear solutions in a fairly good manner. The measured value of the fractional order is the same for both short and long times and is equal to 1,1. The fractional order value 1,1 reveals that methanol transport in the porous catalyst grain occurs in the fast super-diffusive regime, comparing to standard diffusion.
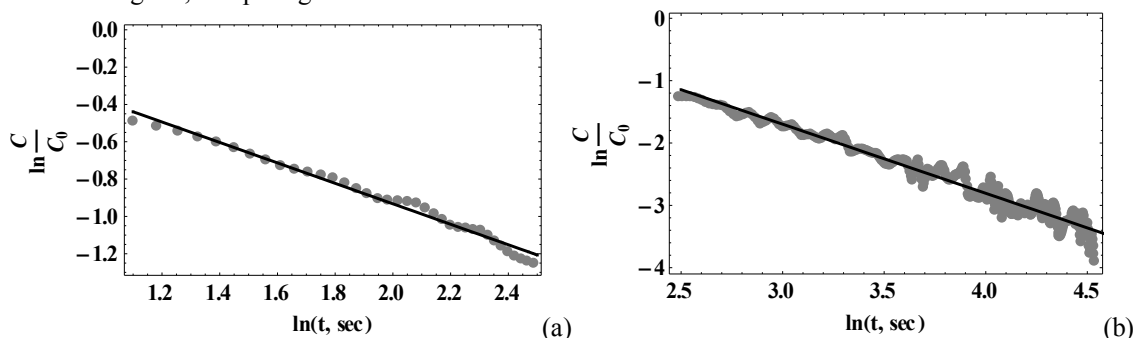

Fig. 2. Linearization of the experimental data for small times according to Eq. (3) (graph (a)) and for large times according to Eq. (4) (graph (b)). For (a) the fitted linear equation is $y = 0,16 – 0,55 \cdot x$, correlation coefficient is 98.5%; for (b) the fitted linear equation is $y = 1,62 – 1,1 \cdot x$, correlation coefficient is 96,0%

The measured values of fractional the order α for the methanol super-diffusion in the H-ZSM-5/alumina catalyst grain, obtained in terms of Caputo fractional integral, demonstrate the value of distribution exponent of random time intervals that methanol molecules stay at one site on the surface of the catalyst grain. As demonstrated by Hilfer [3] mass-conservation law in terms of the fractional diffusion holds only for Caputo fractional integral, because not all continuous time random walks with power-law kernels are equal to the time-fractional diffusion equation. Distribution exponent of random time intervals may be associated with the process of the methanol adsorption on the active acid sites of zeolite and alumina on the catalyst surface.

Conclusions

Experimental data analysis for the methanol transport in H-ZSM-5/alumina catalyst grain demonstrates that methanol mass transfer is acurately described by the time-fractional diffusion equation. The present study shows that methanol transport in the catalyst grain is characterized as superdiffusion, which is faster comparing to standard diffusion. Experimental evidence for the anomalous diffusion of methanol in the H-ZSM-5/alumina catalyst grain presented in our study is important for improving the efficiency of the methanol-to-olefin reaction by keeping the fast methanol transport in the pores of the catalyst grain.

References

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